

Experimental Determination of Contaminant Metal Mobility as a Function of Temperature, Time, and Solution Chemistry

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During the FY96-FY99 funding cycle we examined the uptake of aqueous strontium onto goethite, kaolinite, and amorphous silica surfaces as a function of pH, total strontium, and temperature. Our overall goal was to produce a mechanistic sorption model that can be used in reaction-transport calculations to predict the mobility and attenuation of radioactive strontium (^{90}Sr) in the environment. Our approach was to combine structural information derived from EXAFS analysis together with macroscopic uptake data and surface complexation models to clarify the physical and chemical structure of sorbed complexes. We chose to study these solids because of the prevalence of clays and iron hydroxides in natural systems, and because silica colloids probably form beneath leaking tanks at Hanford as caustic waste is neutralized. We have published the spectroscopic work in two papers in the *Journal of Colloid and Interface Science* [1, 2], and will soon submit a third manuscript to *Geochemical Transactions* [3] combining the sorption and spectroscopic data with a mechanistic complexation model.

Early in the study we learned that strontium sorption was independent of temperature (25 to 80°C). All subsequent work was conducted at room temperature. Below, we focus this summary on three important conclusions from our study.

(i) Strontium sorbs primarily as a hydrated outer-sphere complexes that are stable for several months over the precipitation of pure strontianite, $\text{SrCO}_3(\text{s})$

We collected EXAFS spectra on more than 20 amorphous silica, kaolinite, and goethite samples from pH 4 to 10. With the exception of two goethite samples (see below), the EXAFS analyses suggested that the largest fraction of sorbed strontium on these phases was present as hydrated (i.e., water-ligated) complexes. This interpretation is based on the absence of backscattering atoms beyond the first oxygen shell in the EXAFS spectra. There was no evidence for dehydration of a significant fraction (>50%) of strontium and formation of inner-sphere complexes. We conclusively demonstrated that second-neighbor backscattering would be readily apparent in low-temperature spectra if dehydration occurred based on the analysis of strontium reference compounds [1]. For strontium sorbed to amorphous silica and kaolinite, there was also no evidence in the spectra for backscattering from a carbonate ligand in the presence of dissolved CO_2 . The macroscopic sorption data and equilibrium aqueous speciation are consistent with the EXAFS results. Similar sorption behavior in the presence and absence of dissolved CO_2 .

(ii) Nucleation of incipient $\text{SrCO}_3(\text{s})$ to goethite is tied to carbonate sorption

Limited spectroscopic evidence suggests that the goethite surface may nucleate strontium carbonate precipitation from fairly concentrated solutions ($\text{Sr}_{\text{initial}} = 10^{-3}$ molal). Results to date indicate that nucleation of a precipitate is related to solution pH and to the

sorption of carbonate to the goethite surface (which is dependent on pH), rather than on the saturation state of the solution, and to reaction time. Spectra of samples reacted for short times suggested that $\text{SrCO}_3(\text{s})$ nucleation required a critical concentration of carbonate sorbed to the goethite surface, even though reacting solutions for all samples were supersaturated with respect to $\text{SrCO}_3(\text{s})$. However, kinetic experiments suggested that the strontium carbonate surface precipitate may be a transitory phase. We observed $\text{SrCO}_3(\text{s})$ surface precipitates after four days of reaction, when strontium uptake to goethite was greatest. In a sample aged for 57 days, we observed only outer-sphere complexes and more strontium uptake than for samples aged for shorter times.

(iii) Surface Complexation Model

Our spectroscopic results allow us to constrain the molecular reactions used in the surface complexation models. For amorphous silica and kaolinite, mechanistic models must describe strontium sorption as outer-sphere complexes that retain their primary hydration sheath. Strontium sorption to goethite is more complicated and may require strontium-carbonate surface precipitates or complexes in addition to outer-sphere complexes.

We successfully modeled the uptake of strontium to amorphous silica as an outer-sphere complex over a range of initial strontium concentrations ($[\text{Sr}]_{\text{initial}} = 7 \times 10^{-6}$ to 10^{-3} molal) and pH (6 to 10) at constant ionic strength. We used deprotonation and surface capacitance constants ($\log K_{>\text{SiO}^-} = -2.5$ and $C_1 = C_2 = 6 \text{ Fm}^{-2}$) determined by the direct observation of the pH-dependence of $>\text{SiOH}$ and $>\text{SiO}^-\text{Na}^+$ amorphous silica surface sites using nuclear magnetic resonance spectroscopy [4]. From these values and our experimental uptake data, we have determined outer-sphere sorption constants for strontium, $\log K_{>\text{SiO}^-\text{Sr}^{2+}} = -9.5$, and for sodium, $\log K_{>\text{SiO}^-\text{Na}^+} = -6.6$.

We modeled the uptake of strontium to negatively charged sites on the kaolinite basal plane as an outer-sphere complex ($\log K_{>\text{PO}^-\text{Sr}^{2+}} = 0.0$) over a range of initial strontium concentrations ($[\text{Sr}]_{\text{initial}} = 10^{-5}$ to 10^{-3} molal) and pH (5 to 10) at constant ionic strength. The negative sites on the kaolinite basal plane are due to the isomorphic substitution of Al^{3+} for Si^{4+} in the silica layer. In our model we assumed that the protonation of this site is dependent on pH.

Our efforts to model strontium sorption to goethite as a combination of strontium-carbonate surface precipitates or complexes in addition to outer-sphere complexes was unsuccessful. We suspect that the protonation and deprotonation constants are poorly constrained for goethite because we observed similar strontium uptake to goethite and amorphous silica as a function of pH, even though each mineral has distinct surface properties. General knowledge of mineral surface charge has been derived from the differences in measured and calculated solution pH from acid-base titrations. These experiments are problematic because the measured pH is not a unique measurement of the uptake or release of protons; carbonate speciation, mineral dissolution, and electrolyte sorption all effect solution pH. Sorption constants of fundamental protonation-deprotonation reactions must be well constrained before both carbonate and strontium uptake can be modeled accurately within evidence imposed by spectroscopic observation.

Our renewal proposal picks up where this proposal ended and addresses the ionic strength effects strontium sorption, novel measurement of goethite protonation and deprotonation reactions, solubility and stability of $\text{SrCO}_3(\text{s})$ precipitates identified on goethite surfaces, and application of mechanistic sorption models to column reaction-transport experiments using Hanford sediments.

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